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Structure of 5-[(2,3-Epoxy-3-methyl)butoxy]furo[3,2-g]coumarin

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Abstract. $C_{16}H_{14}O_5$, $M_r = 286.28$, triclinic, $P\bar{1}$, $a = 8.485$ (1), $b = 11.054$ (2), $c = 7.868$ (1) Å, $\alpha = 103.31$ (1), $\beta = 94.97$ (1), $\gamma = 105.88$ (1)°, $V = 681.8$ (2) Å³, $Z = 2$, $D_x = 1.394$ Mg m⁻³, $\lambda(\text{Cu } K\alpha) = 1.54178$ Å, $\mu = 0.775$ mm⁻¹, $F(000) = 300$, room temperature, $R = 0.050$ for 1490 observed reflections. The furocoumarin system is not strictly planar. The pyran ring adopts a very flattened boat conformation. The orientation of the (2,3-epoxy-3-methyl)butoxy substituent is determined by a weak intramolecular C—H...O hydrogen bond.

Introduction. Coumarin compounds have a wide spectrum of biological activity including antithrombotic effects, vasodilating effects on coronary vessels, a tonic influence on capillary blood vessels, reduction in blood pressure, and antispastic and photosensitizing effects. The mechanism of coumarin biological activity is, in most cases, unknown.

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This paper presents results of a structural study of 5-[(2,3-epoxy-3-methyl)butoxy]furo[3,2-g]coumarin (oxypeucedanin), a compound extracted from the roots and fruits of *Angelica archangelica* L. and *Angelica silvestris* L. (Cisowski, 1986), and is part of a systematic study of coumarins and flavonoids extracted from plants of the *Umbelliferae* family.

Experimental. Poor-quality single crystals were grown, with great difficulty, by slow evaporation from acetone; crystal system and approximate cell dimensions were determined from oscillation and Weissenberg photographs; crystal specimen 0.35 × 0.20 × 0.05 mm; Syntex $P2_1$ four-circle diffractometer, graphite-monochromated Cu $K\alpha$ radiation, θ - 2θ scan mode, background and intensity of reflections determined by peak-profile analysis (Lehmann & Larsen, 1974; Jaskólski, 1982); accurate cell parameters refined from setting angles of 15 reflections with $29.7 \leq 2\theta \leq 45.0^\circ$, maximum $(\sin\theta/\lambda) = 0.509$ Å⁻¹, $0 \leq h \leq 10$, $-13 \leq k \leq 13$, $-10 \leq l \leq 10$,

Table 1. *Final fractional coordinates and equivalent isotropic thermal parameters (\AA^2)*

$$U_{\text{eq}} = \frac{1}{3}(U_{11}U_{22}U_{33}).$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
O(1)	-0.3254 (2)	0.0362 (2)	0.8949 (2)	0.0500 (7)
C(2)	-0.3598 (3)	-0.0143 (3)	0.7139 (4)	0.049 (1)
C(3)	-0.2227 (3)	0.0119 (3)	0.6189 (4)	0.048 (1)
C(4)	-0.0682 (3)	0.0758 (3)	0.7022 (3)	0.043 (1)
C(5)	0.1292 (3)	0.1902 (2)	0.9838 (3)	0.0423 (9)
C(6)	0.1525 (3)	0.2355 (3)	1.1687 (3)	0.0456 (9)
C(7)	0.0094 (3)	0.2124 (3)	1.2487 (3)	0.050 (1)
C(8)	-0.1500 (4)	0.1477 (3)	1.1652 (4)	0.051 (1)
C(9)	-0.1667 (3)	0.1039 (3)	0.9844 (4)	0.0448 (9)
C(10)	-0.0319 (3)	0.1231 (2)	0.8917 (3)	0.0395 (9)
C(11)	0.2879 (4)	0.3046 (3)	1.3144 (4)	0.055 (1)
C(12)	0.2203 (4)	0.3171 (3)	1.4607 (4)	0.060 (1)
O(13)	0.0509 (3)	0.2628 (2)	1.4288 (2)	0.0602 (8)
O(14)	0.2488 (2)	0.2050 (2)	0.8794 (2)	0.0492 (7)
C(15)	0.4213 (3)	0.2588 (4)	0.9549 (4)	0.051 (1)
C(16)	0.5126 (3)	0.2832 (3)	0.8078 (4)	0.050 (1)
O(17)	0.5303 (2)	0.4101 (2)	0.7750 (3)	0.0590 (8)
C(18)	0.6780 (3)	0.3783 (3)	0.8366 (4)	0.048 (1)
C(19)	0.7869 (4)	0.3629 (3)	0.6972 (5)	0.068 (1)
C(20)	0.7668 (4)	0.4571 (3)	1.0161 (4)	0.058 (1)
O(21)	-0.5031 (2)	-0.0773 (2)	0.6521 (3)	0.0611 (9)

Table 2. *Bond lengths (\AA) and bond angles ($^\circ$) with e.s.d.'s in parentheses*

O(1)—C(2)	1.378 (3)	C(7)—O(13)	1.373 (3)
O(1)—C(9)	1.382 (3)	C(8)—C(9)	1.373 (4)
C(2)—C(3)	1.436 (4)	C(9)—C(10)	1.403 (4)
C(2)—O(21)	1.216 (3)	C(11)—C(12)	1.326 (5)
C(3)—C(4)	1.333 (3)	C(12)—O(13)	1.373 (4)
C(4)—C(10)	1.437 (3)	O(14)—C(15)	1.435 (3)
C(5)—C(6)	1.402 (3)	C(15)—C(16)	1.482 (5)
C(5)—C(10)	1.404 (3)	C(16)—O(17)	1.454 (4)
C(5)—O(14)	1.359 (3)	C(16)—C(18)	1.468 (3)
C(6)—C(7)	1.404 (4)	O(17)—C(18)	1.464 (4)
C(6)—C(11)	1.451 (3)	C(18)—C(19)	1.504 (5)
C(7)—C(8)	1.368 (4)	C(18)—C(20)	1.488 (4)
C(2)—O(1)—C(9)	122.7 (2)	C(5)—C(10)—C(9)	120.0 (2)
O(1)—C(2)—O(21)	116.3 (3)	C(4)—C(10)—C(9)	117.2 (2)
O(1)—C(2)—C(3)	116.7 (3)	C(4)—C(10)—C(5)	122.8 (2)
C(3)—C(2)—O(21)	127.0 (3)	C(6)—C(11)—C(12)	106.5 (3)
C(2)—C(3)—C(4)	121.7 (3)	C(11)—C(12)—O(13)	113.0 (3)
C(3)—C(4)—C(10)	121.2 (3)	C(7)—O(13)—C(12)	105.6 (2)
C(10)—C(5)—O(14)	114.6 (2)	C(5)—O(14)—C(15)	121.1 (2)
C(6)—C(5)—O(14)	126.5 (2)	O(14)—C(15)—C(16)	106.4 (3)
C(6)—C(5)—C(10)	118.9 (2)	C(15)—C(16)—C(18)	122.6 (3)
C(5)—C(6)—C(11)	138.6 (3)	C(15)—C(16)—O(17)	114.9 (3)
C(5)—C(6)—C(7)	116.6 (2)	O(17)—C(16)—C(18)	60.1 (2)
C(7)—C(6)—C(11)	104.8 (2)	C(16)—O(17)—C(18)	60.4 (2)
C(6)—C(7)—O(13)	110.1 (3)	C(16)—C(18)—O(17)	59.5 (2)
C(6)—C(7)—C(8)	126.7 (2)	O(17)—C(18)—C(20)	115.2 (3)
C(8)—C(7)—O(13)	123.1 (3)	O(17)—C(18)—C(19)	112.5 (3)
C(7)—C(8)—C(9)	114.6 (3)	C(16)—C(18)—C(20)	122.3 (3)
O(1)—C(9)—C(8)	116.6 (3)	C(16)—C(18)—C(19)	118.7 (3)
C(8)—C(9)—C(10)	123.1 (3)	C(19)—C(18)—C(20)	115.2 (3)
O(1)—C(9)—C(10)	120.3 (2)		

two standard reflections measured after every 100 reflections; no variation in intensity. 1791 unique reflections measured, 1490 considered as observed [$I \geq 2\sigma(I)$]. Lp correction but no absorption correction. Structure solved by direct methods with *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978); the best set of phases

enabled location of 20 out of 21 non-H atoms. After three cycles of isotropic and subsequent anisotropic least-squares refinement, a difference synthesis was calculated and the position of the missing C(15) atom found.

Structure refined by full-matrix least squares with *SHELX76* (Sheldrick, 1976), function minimized $\sum w(|F_o| - |F_c|)^2$, $w^{-1} = \sigma^2(F_o) + 0.0002F_o^2$, $\sigma(F_o)$ based on counting statistics. Non-H atoms refined anisotropically, all H atoms placed at their theoretical positions and then refined isotropically with the exception of the H atoms of the methyl groups. These were located from a difference synthesis and not refined. Empirical isotropic extinction parameter x used to correct F_c according to $F_c' = F_c(1 - xF_c^2/\sin\theta)$; x converged at $11(4) \times 10^{-7}$. Final $R = 0.050$, $wR = 0.066$, $S = 3.12$, $(\Delta/\sigma)_{\text{max}} = 0.005$ in final cycle; largest peak in final ΔF map 0.19 , largest hole -0.17 e \AA^{-3} ; total number of refined parameters 223; atomic scattering factors were those incorporated in *SHELX76*. The other computer programs used were: *ORTEP* (Johnson, 1976), *PLUTO78* (Motherwell & Clegg, 1978) and *PARST* (Nardelli, 1983).

Discussion. Final positional parameters and U_{eq} values for non-H atoms are given in Table 1.* Fig. 1 shows a perspective view of the molecule; bond lengths and bond angles are listed in Table 2.

* Lists of structure factors, anisotropic thermal parameters, torsion angles, H-atom parameters, bond lengths and angles involving H atoms and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52997 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

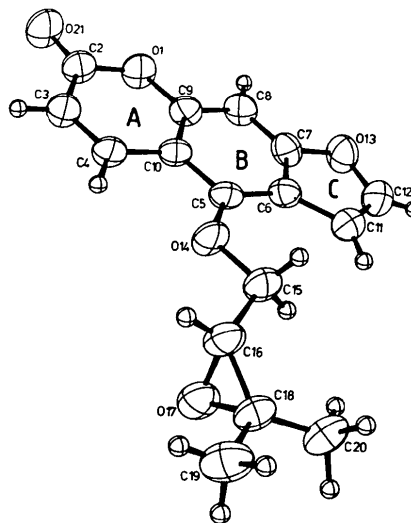


Fig. 1. A perspective view of the molecule.

Table 3. Details of intermolecular hydrogen bonds

C(4)⋯O(13 ⁱ)	3.347 (4) Å	C(12)⋯O(17 ⁱⁱ)	3.211 (4) Å
C(4)—H(41)	0.98 (3) Å	C(12)—H(121)	0.89 (3) Å
H(41)⋯O(13 ⁱ)	2.73 (3) Å	H(121)⋯O(17 ⁱⁱ)	2.47 (3) Å
C(4)—H(41)⋯O(13 ⁱ)	121 (2)°	C(12)—H(121)⋯O(17 ⁱⁱ)	141 (3)°

Symmetry codes: (i) $x, y, z - 1$; (ii) $x, y, z + 1$.

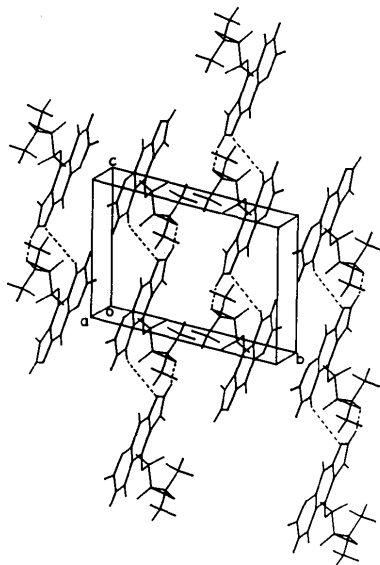


Fig. 2. The molecular packing.

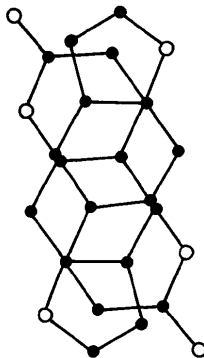


Fig. 3. Projection on the molecular plane of two furocoumarin moieties.

The furocoumarin atoms are nearly coplanar as in other furocoumarin derivatives (see *e.g.* Bideau, Bravic & Desvergne, 1979; Bravic & Bideau, 1978; Dall'Acqua, Benetollo & Bombieri, 1981). The deviations from the mean plane of the three rings range from -0.037 (3) to 0.032 (2) Å, indicating a reasonably planar system. Two bonds in the heterocyclic rings [C(3)—C(4) and C(11)—C(12)] are distinctly double bonded in character with lengths of

1.333 (3) and 1.326 (5) Å, respectively. The conformation around the C(15)—C(16) bond is staggered and the three-membered ring makes a dihedral angle with the furan ring of 97.8 (2)°; the torsion angle O(14)—C(15)—C(16)—O(17) is 87.9 (3)°. The O(14) atom is involved in a weak intramolecular hydrogen bond, C(4)—H(41)⋯O(14), with parameters as follows: C(4)⋯O(14) 2.748 (3), C(4)—H(41) 0.98 (3), H(41)⋯O(14) 2.42 Å and C(4)—H(41)⋯O(14) 98 (2)°. Crystal cohesion is maintained mainly by the weak intermolecular hydrogen bonds C—H⋯O (Table 3, Fig. 2) which connect the molecules into infinite ribbons along the c axis. Moreover, two adjacent ribbons are oriented in such a way that their furocoumarin moieties are connected *via* π donor-acceptor interactions perpendicular to the molecular planes, thus forming dimers with an interplanar distance of 3.41 (2) Å (Fig. 3). Owing to the hindering effect of the (2,3-epoxy-3-methyl)butoxy substituent, infinite stacks of parallel and overlapping molecules cannot be formed; this contrasts with the crystal structures of furo[3,2-*g*]coumarin (Bideau, Bravic & Desvergne, 1979), 3-ethoxycarbonylfuro[3,2-*f*]coumarin (Bravic & Bideau, 1978) and 8-methoxyfuro[3,2-*g*]coumarin (Dall'Acqua, Benetollo & Bombieri, 1981) in which such stacking was observed.

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